

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-223418

(43)Date of publication of application : 11.08.2000

(51)Int.Cl.

H01L 21/205  
// H01L 33/00  
H01S 5/323

(21)Application number : 11-027009

(71)Applicant : NEC CORP

(22)Date of filing : 04.02.1999

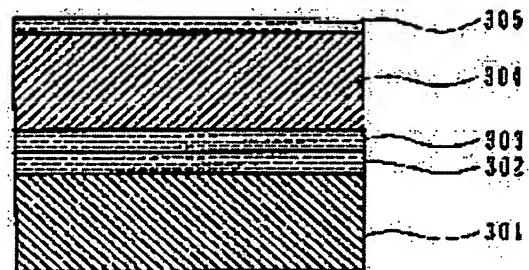
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## (54) GAS-PHASE EPITAXIAL GROWTH METHOD, SEMICONDUCTOR SUBSTRATE, AND MANUFACTURE THEREOF AND HYDRIDE GAS- PHASE EPITAXY DEVICE

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To lessen the growth rate and accelerate the surface migration of molecules if group III atom, by specifying the relation among the growth rate, the growth pressure, and the layer thickness, when growing a second semiconductor layer in second thickness at second growth rate and growth pressure after growing a first semiconductor layer in first thickness at first growth rate and growth pressure on a substrate.

**SOLUTION:** A thin GaN layer 302 is grown at a growth rate of, for example, 4  $\mu\text{m}/\text{h}$  or under by depressurized hydride VPE method on a substrate 301, and then a thick AlGaN layer 304 is grown enough at a growth rate of 4-400  $\mu\text{m}/\text{h}$  by normal pressure hydride VPE method on this GaN layer 2. Here, in the gas-phase epitaxial growth method which grows a second semiconductor layer in thickness  $d_3$  at growth rate  $V_3$  and growth pressure  $P_3$  as it is after growing the first semiconductor layer in thickness  $d_2$  at growth rate  $V_2$  and growth pressure  $P_2$  on the substrate, it is so arranged as to fulfill the conditions of  $V_2 < V_3$ , and besides  $P_2 < P_3$ , and besides  $d_2 < d_3$ .



### LEGAL STATUS

[Date of request for examination] 24.03.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3171180

[Date of registration] 23.03.2001

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase-epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment V2<V3, P2<P3, and the vapor-phase-epitaxial-growth method characterized by fulfilling the conditions which become d2< d3.

[Claim 2] growth temperature T3 of the growth temperature T2 of said 1st semi-conductor layer, and the 2nd semi-conductor layer -- T2<T3 -- the vapor-phase-epitaxial-growth method according to claim 1 characterized by fulfilling conditions.

[Claim 3] The vapor-phase-epitaxial-growth method according to claim 1 or 2 said vapor-phase-epitaxial-growth method is characterized by being a hydride vapor-phase-epitaxial-growth method or an organic metal vapor-phase-epitaxial-growth method.

[Claim 4] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 3 they are. [ to which growth rates V2 and V3 are characterized by fulfilling the conditions which become 3< 400 micrometer/h 4 micrometer/h <V 2< 4 micrometer/h 0 micrometer/h <V, respectively ]

[Claim 5] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 4 they are. [ to which the growth pressures P2 and P3 are characterized by fulfilling the conditions which become 3< 1000 torr 200 torr< P 2< 200 torr 1 torr< P, respectively ]

[Claim 6] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 5 they are. [ which is characterized by the growth thickness d2 and d3 fulfilling the conditions which become 2< 500nm of 0 nm< d, and 3< 1mm of 10 micrometer< d, respectively ]

[Claim 7] the growth temperature T2 and T3 -- respectively -- 400degree-C< T -- 2< 700 degrees C and 700 degrees C -- <-- T3<1200 degree C -- a vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 6 they are. [ which is characterized by fulfilling conditions ]

[Claim 8] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 7 they are. [ to which both said 1st semi-conductor layer and the 2nd semi-conductor layer are characterized by n mold or being both p molds ]

[Claim 9] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 8 they are. [ which is characterized by at least one layer of said 1st semi-conductor layer or the 2nd semi-conductor layer being BX1AlY1GaZ1In1-X1-Y1-Z1N (0 <=X1, Y1, Z1 <=1) ]

[Claim 10] A vapor-phase-epitaxial-growth method given in claim 1 thru/or any of 9 they are. [ which is characterized by for said substrate being sapphire, Si, or GaAs, for at least one layer of said 1st semi-conductor layer being AlX2Ga1-X2N (0 <=X2 <=1), and at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N (0 <=Y2 <=1) ]

[Claim 11] A vapor-phase-epitaxial-growth method given in claim 9 thru/or any of 11 they are. [ which is characterized by for said 1st semi-conductor layer being GaN, AlN, or GaN/AlN superlattice, and said 2nd semi-conductor layer being AlY3Ga1-Y3N (0.05 <=Y3 <=0.5) ]

[Claim 12] The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase-epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment The manufacture approach of the semi-conductor substrate which consists of said 1st semi-conductor layer and 2nd semi-conductor layer which remove said substrate and are obtained from the wafer formed by the vapor-phase-epitaxial-growth method which fulfills V2<V3, P2<P3, and the conditions that become d2< d3.

[Claim 13] Furthermore, the manufacture approach of the semi-conductor substrate according to claim 12 characterized by removing any of said 1st semi-conductor layer or the 2nd semi-conductor layer they are.

[Claim 14] The manufacture approach of a semi-conductor substrate according to claim 12 or 13 that both said 1st semi-conductor layer and the 2nd semi-conductor layer are characterized by n mold or being both p molds.

[Claim 15] The manufacture approach of a semi-conductor substrate given in claim 12 thru/or any of 14 they are. [ which is characterized by at least one layer of said 1st semi-conductor layer or the 2nd semi-conductor layer being BX1AlY1GaZ1In1-X1-Y1-Z1N (0 <=X1, Y1, Z1 <=1) ]

[Claim 16] The manufacture approach of a semi-conductor substrate given in claim 12 thru/or any of 15 they are. [ which is characterized by for said substrate being sapphire, Si, or GaAs, for at least one layer of said 1st semi-conductor layer

being AlX2Ga1-X2N ( $0 \leq X2 \leq 1$ ), and at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y2 \leq 1$ ) ]

[Claim 17] The manufacture approach of a semi-conductor substrate given in claim 12 thru/or any of 16 they are. [ which is characterized by for said 1st semi-conductor layer being GaN, AlN, or GaN/AlN superlattice, and said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y3 \leq 0.5$ ) ]

[Claim 18] The manufacture approach of a semi-conductor substrate given in claim 13 thru/or any of 17 they are. [ to which relation between the thickness d1 of said substrate and the thickness d3 of said 2nd semi-conductor layer is characterized by being  $d1 < d3$  ]

[Claim 19] After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method.  $d2 \dots < \dots d3$  -- the semi-conductor substrate which fulfills conditions -- it is -- said 1st semi-conductor layer or the 2nd semi-conductor layer 3 -- the semi-conductor substrate characterized by at least one layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X1, Y1, Z1 \leq 1$ ).

[Claim 20] After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method. It is the semi-conductor substrate which fulfills the becoming conditions  $d2 < d3$ , and said substrate is sapphire, Si, or GaAs. The conductor characterized by for at least one layer of said 1st semi-conductor layer being AlX2Ga1-X2N ( $0 \leq X2 \leq 1$ ), and at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y2 \leq 1$ ) -- a substrate.

[Claim 21] After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method. The semi-conductor substrate characterized by being the semi-conductor substrate which fulfills the becoming conditions  $d2 < d3$ , for said 1st semi-conductor layer being GaN, AlN, or GaN/AlN superlattice, and said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y3 \leq 0.5$ ).

[Claim 22] A semi-conductor substrate given in claim 19 thru/or any of 21 they are. [ to which relation between the thickness d1 of said substrate and the thickness d3 of said 2nd semi-conductor layer is characterized by being  $d1 < d3$  ]

[Claim 23] A semi-conductor substrate given in claim 19 thru/or any of 22 they are. [ to which both said 1st semi-conductor layer and the 2nd semi-conductor layer are characterized by n mold or being both p molds ]

[Claim 24] Hydride vapor phase epitaxy equipment characterized by making growth possible by 10 or more torrs the pressure of less than 800 torr while making possible crystal growth which has interpolation tubing made from sapphire installed so that the coil or substrate made from sapphire might be surrounded, and contains aluminum.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the vapor-phase epitaxial-growth method of semi-conductors, such as nitride system group-III-V-semiconductor film, such as high quality, and a GaN substrate excellent in mass-production nature, an AlGaN substrate, the manufacture approach of a semi-conductor substrate, a semi-conductor substrate, and its growth equipment with respect to a vapor-phase epitaxial-growth method, the manufacture approach of a semi-conductor substrate, a semi-conductor substrate, and hydride vapor phase epitaxy (VPE) equipment.

[0002]

[Description of the Prior Art] In recent years, development of the blue of short wavelength and the semiconductor laser diode (LD) of ultraviolet-rays luminescence is made from the demand of the densification of the record over an optical disk or a magneto-optic disk, and playback, and high-resolution-izing. For example, 93 pages of the Nikkei electronics No. 602 in February, 1994 have description of the blue light emitting diode by Mr. Nakamura of Nichia Chemical Industries.

[0003] Since forbidden-band width of face is moreover a direct transition mold as greatly as 3.4eV, GaN which is a nitride system group III-V semiconductor attracts attention as blue and a charge of ultraviolet-rays light emitting device material. Conventionally, many sapphire is used for nitride system group-III-V-semiconductor crystal growth as a substrate ingredient. growth of the GaN film to a silicon-on-sapphire top -- a 900-1100-degree C elevated temperature -- organic metal vapor phase epitaxial growth (MOVPE) -- law and molecular beam epitaxy (MBE) -- it is carried out by law. Although the film which already has the crystal quality of a device level is obtained, when the lattice constant differs from the coefficient of thermal expansion, silicon on sapphire and a GaN epitaxial layer have the problem of a defect being generated or a crack occurring, and are reducing the property and dependability of a component.

[0004] Furthermore, since [ that it is lacking in it ] workability of silicon on sapphire is bad to cleavage, formation and chip-izing of a mirror side required for LD are difficult for it to it. Moreover, since sapphire is insulation electrically, it needs complicated processes, such as selective etching, for electrode formation of a component. Since a GaN thick-film substrate does not have the problem of a defect being generated when the GaN epitaxial layer, the lattice constant, and the coefficient of thermal expansion are in agreement, or a crack occurring, it is an ideal substrate ingredient. By this, the resonator end face of LD can be formed by cleavage, an electrode can be formed in the rear face of a substrate, and the property and dependability of a component can be raised.

[0005] However, in order to manufacture the thick-film substrate of GaN, the approach generally used for manufacture of Si substrate, a GaAs substrate, etc. cannot be used according to the vapor pressure of nitrogen being high. as the growth approach of GaN -- MOCVD -- law and MBE -- law -- the hydride vapor phase epitaxy (VPE) which uses a hydride (hydride) for except as a raw material -- law gets to know -- having -- \*\*\*\* -- JP,10-173288,A -- "the growth approach of a nitride system group-III-V-semiconductor layer, and the manufacture approach of a nitride system group-III-V-semiconductor substrate" -- invention is indicated. According to this hydride VPE method, since the GaN layer of the thickness of a number - 100 micrometers of numbers can be grown up by ordinary pressure on silicon on sapphire in 1 hour, it is considered one of the effective approaches which manufactures a GaN substrate.

[0006] However, since the GaN substrate obtained by this approach had crystallinity and a bad surface state or grew at right angles [ a GaN layer ] to a substrate, and aslant, its quality was inadequate for using as a substrate. the reason -- the ordinary pressure hydride VPE -- it is because the growth rate of law is large, so outstanding GaN of crystal quality is not obtained. Moreover, if an AlGaN substrate is obtained, since AlGaN of the high quality of the same aluminum presentation as a substrate can be used for the cladding layer of LD, from LD on a GaN substrate, light can be confined in a barrier layer still more efficiently, and the property of LD can be raised greatly.

[0007] however, the ordinary pressure hydride VPE -- since the growth rate of law is large, the migration on the front face of a crystal of the raw material containing aluminum, such as chlorination aluminum (AlCl<sub>3</sub>), becomes very small, and the epitaxial crystal of high quality is not obtained. There was a problem that the raw material containing aluminum, such as chlorination aluminum, moreover corroded a quartz coil by the hydride VPE method, and insurance and the stable growth were difficult. Moreover, the oxygen which came out of the quartz coil was incorporated by the epitaxial layer, and the problem of reducing crystal quality also had it.

[0008]

[Problem(s) to be Solved by the Invention] the fault of the conventional technique which the purpose of this invention described above -- improving -- especially -- the reduced pressure hydride VPE -- by law A growth rate becomes small, and the surface migration of an III group raw material molecule is promoted, and the crystal of good quality is obtained, and by the continuous ordinary pressure hydride VPE method on it The vapor-phase epitaxial-growth method of the new

semi-conductor which was quality and was excellent in mass-production nature which made it possible to grow up GaN and AlGaN with a big growth rate, the manufacture approach of a semi-conductor substrate, a semi-conductor substrate, and its growth equipment are offered.

[0009]

[Means for Solving the Problem] Fundamentally, this invention adopts a technical configuration which was indicated below in order to attain the above-mentioned purpose. Namely, the 1st mode of the vapor-phase-epitaxial-growth method concerning this invention The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase-epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment It is what is characterized by fulfilling  $V_2 < V_3$ ,  $P_2 < P_3$ , and the conditions that become  $d_2 < d_3$ . \*\* and the 2nd mode It is what is characterized by fulfilling conditions. growth temperature T3 of the growth temperature T2 of said 1st semi-conductor layer, and the 2nd semi-conductor layer --  $T_2 < T_3$  -- \*\* and the 3rd mode It is that to which said vapor-phase-epitaxial-growth method is characterized by being a hydride vapor-phase-epitaxial-growth method or an organic metal vapor-phase-epitaxial-growth method. \*\* and the 4th mode Growth rates V2 and V3 are what is characterized by fulfilling the conditions which become  $3 < 400$  micrometer/h 4 micrometer/h  $< V_2 < 4$  micrometer/h 0 micrometer/h  $< V_3$ , respectively. \*\* and the 5th mode The growth pressures P2 and P3 are what is characterized by fulfilling the conditions which become  $3 < 1000$  torr 200 torr  $< P_2 < 200$  torr 1 torr  $< P_3$ , respectively. \*\* and the 6th mode The growth thickness d2 and d3 is what is characterized by fulfilling the conditions which become  $2 < 500$ nm of 0 nm  $< d_2$ , and  $3 < 1$ mm of 10 micrometer  $< d_3$ , respectively. \*\* and the 7th mode It is what is characterized by fulfilling conditions. the growth temperature T2 and T3 -- respectively --  $400$ degree-C  $< T_2 < 700$  degrees C and 700 degrees C --  $< T_3 < 1200$  degree C -- \*\* and the 8th mode Both said 1st semi-conductor layer and the 2nd semi-conductor layer are what is characterized by n mold or being both p molds. \*\* and the 9th mode It is what is characterized by at least one layer of said 1st semi-conductor layer or the 2nd semi-conductor layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ). Said substrate of \*\* and the 10th mode is sapphire, Si, or GaAs. At least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). \*\* and the 11th mode Said 1st semi-conductor layer is GaN, AlN, or GaN/AlN superlattice, and it is characterized by said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ).

[0010] The 1st mode of the manufacture approach of the semi-conductor substrate concerning \*\* and this invention The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase-epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment It is what consists of said 1st semi-conductor layer and 2nd semi-conductor layer which remove said substrate and are obtained from the wafer formed by the vapor-phase-epitaxial-growth method which fulfills  $V_2 < V_3$ ,  $P_2 < P_3$ , and the conditions that become  $d_2 < d_3$ . It is what is characterized by \*\* and the 2nd mode removing further any of said 1st semi-conductor layer or the 2nd semi-conductor layer they are. \*\* and the 3rd mode Both said 1st semi-conductor layer and the 2nd semi-conductor layer are what is characterized by n mold or being both p molds. \*\* and the 4th mode It is what is characterized by at least one layer of said 1st semi-conductor layer or the 2nd semi-conductor layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ). Said substrate of \*\* and the 5th mode is sapphire, Si, or GaAs. At least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). \*\* and the 6th mode Said 1st semi-conductor layer is GaN, AlN, or GaN/AlN superlattice. It is characterized by said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ), and \*\* and the 7th mode are characterized by the relation between the thickness d1 of said substrate and the thickness d3 of said 2nd semi-conductor layer being  $d_1 < d_3$ .

[0011] The 1st mode of the semi-conductor substrate concerning \*\* and this invention After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method. It is what is characterized by at least one layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ).  $d_2 < d_3$  -- the semi-conductor substrate which fulfills conditions -- it is -- said 1st semi-conductor layer or the 2nd semi-conductor layer 3 -- \*\* and the 2nd mode After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method. It is the semi-conductor substrate which fulfills the becoming conditions  $d_2 < d_3$ , and said substrate is sapphire, Si, or GaAs. At least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). \*\* and the 3rd mode After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase-epitaxial-growth method. It is the semi-conductor substrate which fulfills the becoming conditions  $d_2 < d_3$ , and said 1st semi-conductor layer is GaN, AlN, or GaN/AlN superlattice. It is what is characterized by said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ). \*\* and the 4th mode Relation between the thickness d1 of said substrate and the thickness d3 of said 2nd semi-conductor layer is characterized by being  $d_1 < d_3$ , and, as for both \*\* and the 5th mode, said 1st semi-conductor layer and the 2nd semi-conductor layer are characterized by n mold or being both p molds.

[0012] The mode of the hydride vapor phase epitaxy equipment concerning \*\* and this invention has interpolation tubing made from sapphire installed so that the coil or substrate made from sapphire might be surrounded, and it is characterized by making growth possible by 10 or more torrs the pressure of less than 800 torr while it makes crystal growth

containing aluminum possible.

[0013]

[Embodiment of the Invention] the semi-conductor substrate concerning this invention -- the c-th page silicon-on-sapphire 301 top -- the reduced pressure hydride VPE, after growing up the thin GaN layer 302 with the growth rate of 4 or less micrometer/h by law this GaN layer 2 top -- the ordinary pressure hydride VPE -- the crystal growth method for growing up the larger and AlGaN [ than 4 micrometer/h ] layer 304 thick enough at the growth rate of 400 or less micrometer/h by law -- or the AlGaN substrate which removes c-th page silicon on sapphire 1 by etching, and consists of a GaN layer 302 and an AlGaN layer 304 -- or It is hydride VPE equipment which can grow by 10 or more torrs the pressure of less than 800 torr the crystal containing aluminum which has the AlGaN substrate which consists only of an AlGaN layer 304, interpolation tubing made from sapphire, or a coil made from sapphire can grow up to be.

[0014] By the reduced pressure hydride VPE method, a growth rate becomes small, and the surface migration of III group raw material molecules, such as aluminum, is promoted, and the crystal of good quality is obtained. the \*\* which does not take out an epitaxial substrate out of equipment moreover -- continuing -- a pressure -- large -- carrying out -- the ordinary pressure hydride VPE -- by using law, AlGaN can be grown up with a big growth rate, and the AlGaN substrate of high quality is obtained efficiently.

[0015]

[Example] Below, the example of the vapor-phase-epitaxial-growth method of the semi-conductor concerning this invention, the manufacture approach of a semi-conductor substrate, a semi-conductor substrate, and its growth equipment is explained at a detail, referring to a drawing. The side elevation and front view of hydride VPE equipment of this invention are shown in drawing 1 and drawing 2.

[0016] The hydride VPE equipment of the 1st example of this invention The coil 100 made from sapphire, and the interpolation tubing 101 made from sapphire formed in the coil 100 made from sapphire, The substrate operating rod 102 which puts the substrate in the interpolation tubing 101 made from sapphire into a deposition chamber, is made to move to a standby room, or is operated, The rotary pump 103 prepared in the exhaust port 116, and a pressure regulating valve 104, The substrate holder 105 with a heater operated with the substrate operating rod 102, The substrate 106 fixed to the substrate holder 105, and the heating heater 107 formed so that the coil 100 made from sapphire might be surrounded, In order to introduce gas in the diaphragm 109 made from sapphire for dividing the standby room 108 prepared in the interpolation tubing 101 made from sapphire, and said standby room 108 and deposition chamber, and the interpolation tubing 101 made from sapphire, The gas inlet 110, the gas installation tubing 111, and the gas inlet 112 which were established in one edge of the interpolation tubing 101, The high grade Ga source 113 of a deposition chamber, and the raw material boat 114 with a heater which contains the source, It consists of a deposition chamber 115, an exhaust port 116 established in the other-end section of the interpolation tubing 101, a bottom plate 200 made from sapphire prepared in the pars basilaris ossis occipitalis of the interpolation tubing 101 made from sapphire, and the high grade aluminum source 202 of a deposition chamber 115.

[0017] A gas inlet 110 and the gas installation tubing 111 are the gas inlets and gas installation tubing for introducing ammonia gas and nitrogen gas. A gas inlet 112 is a gas inlet which introduces HCl gas and hydrogen gas. Various kinds of gas supply volume is controlled by the flowmeter and the control valve. Substrates are substrates, such as sapphire, silicon, and GaAs. In n dopant raw material, it is SiH4. SiH2 Cl2 Gas is used and it is Mg (CH3)2 in p dopant raw material. MgCl2 It uses and supplies through the gas installation tubing 111.

[0018] Using the coil 100 made from sapphire, the interpolation tubing 101, a diaphragm 109, and a diaphragm 205, using two kinds of solid-state raw materials, the high grade Ga source 113 and the high grade aluminum source 202, the hydride VPE equipment of this invention is constituted so that the temperature of the high grade Ga source 113 and the high grade aluminum source 202 can be independently controlled by the heating heater 107 and the raw material boat 114 with a heater, and it can control substrate temperature by the substrate holder 105 with a heater from a room temperature to 1200 degrees C. Furthermore, a rotary pump 103 and a pressure regulating valve 104 constitute the pressure in the coil 100 made from sapphire from 10 or more torrs the pressure range of 800 or less torr possible [ accommodation ].

[0019] the inside of the coil 100 made from sapphire is divided into the standby room 108 and a deposition chamber 115 with the diaphragm 109 made from sapphire -- having -- \*\*\*\* -- the substrate operating rod 102 -- using -- the deposition chamber 115 from the standby room 108 -- or the location of a substrate 106 is freely changeable conversely. The high grade Ga source 113 and the high grade aluminum source 202 react, the HCl gas introduced into the deposition chamber 115 from the gas inlet 112 (206 and 207 showed at drawing 2 ) generates a gallium chloride (GaCl3) and an aluminum chloride (AlCl3), and it is carried to a substrate front face with hydrogen gas, and reacts on the ammonia gas and the substrate front face which are supplied from the gas installation tubing 111, and AlGaN grows. aluminum presentation and the growth rate of AlGaN are decided by temperature of the flow rate of HCl gas and the high grade Ga source 113 which were introduced from the gas inlet 206 and the gas inlet 207, and the high grade aluminum source 202.

[0020] Below, the growth approach of this invention by the above-mentioned growth equipment is explained. Silicon on sapphire 106 is installed in the standby room 108, and where nitrogen gas is introduced, substrate temperature is raised from a gas inlet 110 to growth temperature. If the flow rate of the pressure within a reaction, a gallium chloride, or an aluminum chloride is stabilized, it will grow up to be a deposition chamber 115 by changing the location of a substrate 106 from the standby room 108. When growing up the semi-conductor layer from which a presentation differs, after once moving a substrate to the standby room 108, changing the flow rate and pressure of a hydrogen flow rate, a gallium chloride, or an aluminum chloride and stabilizing a flow rate and a pressure, it grows up by returning to a deposition chamber 115 again. Thus, GaN and AlN can grow similarly. When substrate temperature is high and an epitaxial substrate is in the standby room 108, ammonia gas is introduced and the nitrogen omission from a substrate is prevented.

[0021] The epitaxial substrate of the 2nd example of this invention is shown in drawing 3. This epitaxial substrate Silicon on sapphire 301 with a thickness of 100 micrometers, The undoping GaN thin film layer 302 of reduced pressure low-temperature low-speed growth with a thickness of 50nm, It consists of the n-aluminum0.2 Ga0.8 N thin film layer 303 of reduced pressure elevated-temperature low-speed growth with a thickness of 100nm, a n-aluminum0.2 Ga0.8 N thick-film layer 304 of ordinary pressure elevated-temperature high-speed growth with a thickness of 200 micrometers, and a n-GaN thin film protective layer 305 of ordinary pressure elevated-temperature medium-speed growth with a thickness of 10nm. n concentration is  $5 \times 10^{17} \text{ cm}^{-3}$ .

[0022] Time amount change of the growth conditions of the 2nd example of this invention is shown in drawing 5. The conditions of reduced pressure low-temperature low-speed growth are the growth temperature of 500 degrees C, growth pressure 50torr, and growth rate 0.1 micrometer/h. The conditions of reduced pressure elevated-temperature medium-speed growth are the growth temperature of 1100 degrees C, growth pressure 50torr, and growth rate 1 micrometer/h. The conditions of ordinary pressure elevated-temperature high-speed growth are the growth temperature of 1100 degrees C, growth pressure 760torr, and growth rate 60 micrometer/h. If growth temperature goes up to 1100 degrees C from 500 degrees C, disassembly of a raw material will progress and a growth rate will become large. The temperature of 800 degrees C and the high grade aluminum source 202 of the temperature of the high grade Ga source 113 is 900 degrees C.

[0023] The grown method of the 2nd example of the above has the description in the point of increasing growth temperature from reduced pressure low-temperature low-speed growth to reduced pressure elevated-temperature medium-speed growth, and the description is in the point of increasing [ ordinary pressure elevated-temperature high-speed growth ] a pressure and a growth rate from reduced pressure elevated-temperature medium-speed growth to coincidence, further. NH<sub>3</sub> at the time of reduced pressure growth A flow rate is [ the flow rate of HCl to 0.5 cca part for /and aluminum of the flow rate of HCl to 60 cca part for /and Ga ] a part for 0.1 cc/. NH<sub>3</sub> at the time of ordinary pressure growth A flow rate is [ the flow rate of HCl to five cca part for /and aluminum of the flow rate of HCl to 600 cca part for /and Ga ] a part for one cc/.

[0024] Each near partial pressure of gas in ordinary pressure (760torr) growth is H<sub>2</sub>. Partial pressure 734torr and NH<sub>3</sub> Partial pressure 20torr, GaCl<sub>3</sub> partial-pressure 5torr, and AlCl<sub>3</sub> It is partial pressure 1torr. Each near partial pressure of gas in reduced pressure (50torr) growth is H<sub>2</sub>. Partial pressure 47torr and NH<sub>3</sub> Partial pressure 2torr and GaCl<sub>3</sub> Partial pressure 0.5torr and AlCl<sub>3</sub> It is partial pressure 0.1torr.

[0025] The AlGaN substrate of the 2nd example of this invention is shown in drawing 4. The AlGaN substrate of the 2nd example removes silicon on sapphire 301 and the GaN thin film layer 302 of reduced pressure low-temperature medium-speed growth by etching from the above-mentioned epitaxial substrate. The temperature of 300 degrees C performs etching by the etchant of phosphoric acid:sulfuric-acid =2:3. The AlGaN substrate of the 2nd example is [ the n-aluminum0.2 Ga0.8 N thin film layer 401 of reduced pressure elevated-temperature medium-speed growth with a thickness of 100nm, and ] 200 micrometers in thickness. It consists of a n-aluminum0.2 Ga0.8 N thick-film layer 402 of ordinary pressure elevated-temperature high-speed growth, and a n-GaN thin film protective layer 403 of ordinary pressure elevated-temperature medium-speed growth with a thickness of 10nm.

[0026] This invention is not restricted to the detail of the above-mentioned example. For example, a semi-conductor layer does not necessarily need to be a nitride and can carry out an InGaAs substrate etc. by the approach of this invention. Moreover, the detail of growth conditions can be optimized on condition that the range shown below. For example, a growth rate can be enlarged or a growth pressure can be optimized. It is also possible to make structure of a semi-conductor layer into a superstructure. There is especially no limit to a substrate and it can be applied also with a substrate for selective growth which quartz glass was patternized by silicon on sapphire and has deposited on it. aluminum presentation of the AlGaN substrate of this invention can be chosen freely. Not only an AlGaN substrate but a GaN substrate or an AlN substrate may be used. Moreover, the substrate of this invention can be used also as the substrate and heat sink ingredient not only an optical device but for electron devices.

[0027] The coil and interpolation tubing of hydride vapor growth equipment of this invention are a quartz SiO<sub>2</sub>. Not but, sapphire aluminum 2O<sub>3</sub> Since it has done, there is corrosion resistance in an elevated temperature to chlorination aluminum etc. Therefore, also by the elevated-temperature growth for which growth temperature, such as AlGaN, exceeds 1000 degrees C, since it is not corroded, there is also no mixing of oxygen and the semi-conductor film of high quality can be produced safely.

[0028] The 2nd example of drawing 4 is a n-aluminum0.2 Ga0.8 N thick-film substrate with a thickness of 200 micrometers. Since the n-aluminum0.2 Ga0.8 N thin film layer 401 with a thickness [ of the 2nd example ] of 100nm is reduced pressure elevated-temperature medium-speed growth, the surface migration of aluminum is promoted and it serves as film of high quality. 200 micrometers in thickness which grew after that Although the n-aluminum0.2 Ga0.8 N thick-film layer 402 has a large growth rate, since the crystal quality of a substrate is good, there is an operation which serves as film of high quality comparatively.

[0029] The hydride VPE of ordinary pressure has the description which a growth rate can take especially. By this invention, since the growth rate was as large as 60 micrometer/h, the thick-film substrate of 200-micrometer thickness was obtained in about 3 hours. The n-GaN thin film protective layer 403 with a thickness of 10nm has the operation which makes removal of an oxide film easy, when growing up LD of an AlGaN system on it. Thus, the vapor-phase-epitaxial-growth method concerning this invention The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase-epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment It is what is characterized by fulfilling V2<V3, P2<P3, and the conditions that become d2<d3. growth temperature T3 of \*\*, the growth temperature T2 of said 1st semi-

conductor layer, and the 2nd semi-conductor layer -- T2<T3, although it is characterized by fulfilling conditions and \*\* and said vapor-phase epitaxial-growth method used the hydride vapor-phase epitaxial-growth method You may make it make it grow up by the organic metal vapor-phase epitaxial-growth method.

[0030] Growth rates V2 and V3 are characterized by the vapor-phase epitaxial-growth method concerning \*\* and this invention fulfilling the conditions which become  $3 < 400 \text{ micrometer/h}$   $4 \text{ micrometer/h} < V_2 < 4 \text{ micrometer/h}$   $0 \text{ micrometer/h} < V_3$ , respectively. In addition, in an artificer's experimental result, the maximum growth rates from which the maximum growth rates from which the crystal of high quality was obtained are 4 micrometer/h, it is ordinary pressure growth, and the crystal of high quality was obtained by reduced pressure growth were 400 micrometer/h.

[0031] \*\* and the growth pressures P2 and P3 are characterized by fulfilling the conditions which become  $3 < 1000 \text{ torr}$   $200 \text{ torr} < P_2 < 200 \text{ torr}$   $1 \text{ torr} < P_3$ , respectively, and the crystal of high quality was obtained only in the above-mentioned range in an artificer's experimental result. \*\* and growth thickness d2 and d3 are characterized by fulfilling the conditions which become  $2 < 500 \text{ nm}$  of  $0 \text{ nm} < d_2$ , and  $3 < 1 \text{ mm}$  of  $10 \text{ micrometer} < d_3$ , respectively.

[0032] In addition, when a thing with a thickness of 0.05-0.5 micrometers is used as a buffer layer (thickness d2) of low-temperature growth in the case of a GaN system, the epitaxial crystal of high quality is \*\*\*\*\* most. \*\*, the growth temperature T2, and T3 -- respectively -- 400degree-C<T --  $2 < 700 \text{ degrees C}$  and  $700 \text{ degrees C} < T_3 < 1200 \text{ degree C}$  -- it is characterized by fulfilling conditions.

[0033] In the experiment, when the buffer layer was grown up in the 400 degree-C<T2<700 degree C temperature requirement, two-dimensional-ization of a crystal advanced and the epitaxial crystal with a flat front face was obtained. A crystal with \*\* and T3 good also when N atom slips out of a GaN layer, there is an inclination for a good crystal not to be obtained, above 1200 degrees C and T3 is 700 degrees C or less on the other hand was not obtained.

[0034] Both \*\*, said 1st semi-conductor layer, and the 2nd semi-conductor layer may be characterized by n mold or being both p molds, and at least one layer of \*\*, said 1st semi-conductor layer, or the 2nd semi-conductor layer may be BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ). Furthermore, said substrate is sapphire, Si, or GaAs, and at least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). \*\* and said 1st semi-conductor layer may be GaN, AlN, or GaN/AlN superlattice, and said 2nd semi-conductor layer may be AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ).

[0035] The manufacture approach of the semi-conductor substrate concerning \*\* and this invention The 1st semi-conductor layer which consists of at least one layer on the substrate of thickness d1 on the growth conditions of a growth rate V2 and the growth pressure P2 thickness d2 After making it grow up, In a vapor-phase epitaxial-growth method including the process into which the 2nd semi-conductor layer which consists of at least one layer on the growth conditions of a growth rate V3 and the growth pressure P3 is grown up thickness d3, without taking out said substrate out of equipment It is what consists of said 1st semi-conductor layer and 2nd semi-conductor layer which remove said substrate and are obtained from the wafer formed by the vapor-phase epitaxial-growth method which fulfills  $V_2 < V_3$ ,  $P_2 < P_3$ , and the conditions that become  $d_2 < d_3$ . They are \*\* and the thing further characterized by removing any of said 1st semi-conductor layer or the 2nd semi-conductor layer they are. It is that to which both \*\*, said 1st semi-conductor layer, and the 2nd semi-conductor layer are characterized by n mold or being both p molds. It is what is characterized by at least one layer of \*\*, said 1st semi-conductor layer, or the 2nd semi-conductor layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ). \*\* and said substrate are sapphire, Si, or GaAs, and at least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). \*\* and said 1st semi-conductor layer are GaN, AlN, or GaN/AlN superlattice. It is characterized by said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ), and relation between the thickness d1 of \*\* and said substrate and the thickness d3 of said 2nd semi-conductor layer is characterized by being  $d_1 < d_3$ .

[0036] The semi-conductor substrate concerning \*\* and this invention the 1st semi-conductor layer thickness d2 on the substrate of thickness d1 After making it grow up, The 2nd semi-conductor layer grows up thickness d3 by the vapor-phase epitaxial-growth method. It is characterized by at least one layer being BX1AlY1GaZ1In1-X1-Y1-Z1N ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ), and \*\*. d2 --  $< d_3$  -- the semi-conductor substrate which fulfills conditions -- it is -- said 1st semi-conductor layer or the 2nd semi-conductor layer 3 -- After growing up the 1st semi-conductor layer thickness d2 on the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase epitaxial-growth method. It is the semi-conductor substrate which fulfills the becoming conditions  $d_2 < d_3$ , and said substrate is sapphire, Si, or GaAs. At least one layer of said 1st semi-conductor layer is AlX2Ga1-X2N ( $0 \leq X_2 \leq 1$ ). It is what is characterized by at least one layer of said 2nd semi-conductor layer being AlY2Ga1-Y2N ( $0 \leq Y_2 \leq 1$ ). After growing up the 1st semi-conductor layer thickness d2 on \*\* and the substrate of thickness d1, the 2nd semi-conductor layer grows up thickness d3 by the vapor-phase epitaxial-growth method. It is the semi-conductor substrate which fulfills the becoming conditions  $d_2 < d_3$ , and said 1st semi-conductor layer is GaN, AlN, or GaN/AlN superlattice. It is what is characterized by said 2nd semi-conductor layer being AlY3Ga1-Y3N ( $0.05 \leq Y_3 \leq 0.5$ ). Relation between the thickness d1 of \*\* and said substrate and the thickness d3 of said 2nd semi-conductor layer is characterized by being  $d_1 < d_3$ , and both \*\*, said 1st semi-conductor layer, and the 2nd semi-conductor layer are characterized by n mold or being both p molds.

[0037] The mode of the hydride vapor phase epitaxy equipment concerning \*\* and this invention has interpolation tubing made from sapphire installed so that the coil or substrate made from sapphire might be surrounded, and it is characterized by making growth possible by 10 or more torrs the pressure of less than 800 torr while it makes crystal growth containing aluminum possible.

[0038]

[Effect of the Invention] The grown method of this invention can produce efficiently the n-AlGaN thick-film substrate of

high quality. \*\* and the hydride vapor growth equipment of this invention can produce the semi-conductor film of the high quality containing aluminum safely. If sequential formation of the barrier layer of the multiplex quantum well of a n-aluminum0.2 Ga0.8 N clad, GaN, or InGaN/GaN, a p-aluminum0.2 Ga0.8 N clad, and the p-GaN contact layer is carried out and p electrode and n electrode are attached on the n-aluminum0.2 Ga0.8 N thick-film substrate of this invention, LD of an AlGaN system will be obtained. Since optical confinement and eye carrier \*\*\*\*\* are superior to the thing of a GaN substrate, LD of an AlGaN system has high luminous efficiency, and outstanding LD with a low threshold current value is obtained. Since there is also little distortion by the barrier layer and a heat dissipation property is also good, the dependability of the component in continuous oscillation improves. Since-izing can be carried out [ luminescence wavelength nearby short wavelength ], there is an advantage which can improve the recording density of an optical disk.

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[Translation done.]

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

[Drawing 1] It is the side elevation of the hydride VPE equipment which is the 1st example of this invention.

[Drawing 2] It is the front view of the hydride VPE equipment which is the 1st example of this invention.

[Drawing 3] It is the sectional view of the epitaxial substrate of the 2nd example of this invention.

[Drawing 4] It is the sectional view of the AlGaN substrate of the 2nd example of this invention.

[Drawing 5] It is the graph which shows time amount change of the growth conditions of the 2nd example of this invention.

**[Description of Notations]**

100 Coil made from Sapphire

101 Interpolation Tubing made from Sapphire

102 Substrate Operating Rod

103 Rotary Pump

104 Pressure Regulating Valve

105 Substrate Holder

106 Substrate

108 Standby Room

109 Diaphragm made from Sapphire

110 Gas Inlet

111 Gas Installation Tubing

112 Gas Inlet

113 High Grade Ga Source

114 Raw Material Boat

115 Deposition Chamber

116 Exhaust Port

200 Bottom Plate made from Sapphire

202 High Grade Aluminum Source Source

301 Silicon on Sapphire

302 GaN Thin Film Layer of Reduced Pressure Low-temperature Low-speed Growth

303 N-aluminum0.2 Ga0.8 N Thin Film Layer of Reduced Pressure Elevated-Temperature Medium-Speed Growth

304 N-aluminum0.2 Ga0.8 N Thick-Film Layer of Ordinary Pressure Elevated-Temperature High-Speed Growth

305 N-GaN Thin Film Protective Layer of Ordinary Pressure Elevated-Temperature Medium-Speed Growth

401 N-aluminum0.2 Ga0.8 N Thin Film Layer of Reduced Pressure Elevated-Temperature Medium-Speed Growth

402 N-aluminum0.2 Ga0.8 N Thick-Film Layer of Ordinary Pressure Elevated-Temperature High-Speed Growth

403 N-GaN Thin Film Protective Layer of Ordinary Pressure Elevated-Temperature Medium-Speed Growth

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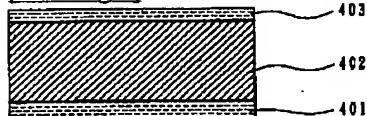
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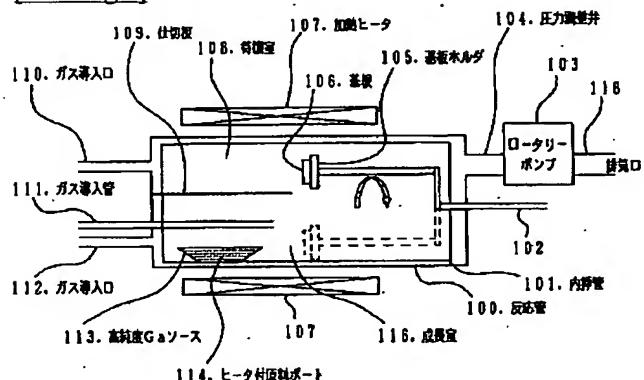
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## DRAWINGS

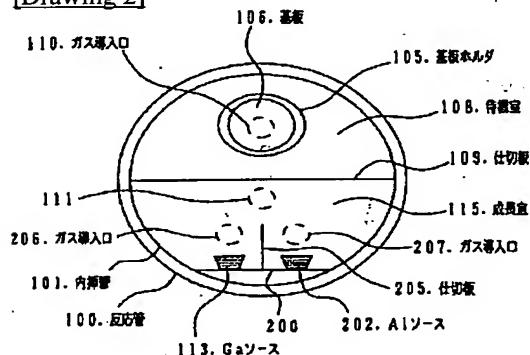
## [Drawing 5]



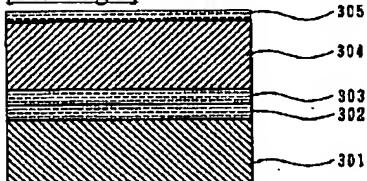
## [Drawing 1]



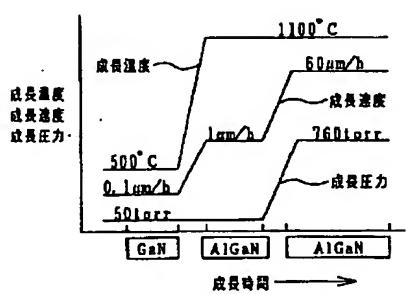
## [Drawing 2]



## [Drawing 3]



## [Drawing 4]



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[Translation done.]

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2000-223418

(P2000-223418A)

(43)公開日 平成12年8月11日 (2000.8.11)

(51)Int.Cl.  
H 01 L 21/205  
// H 01 L 33/00  
H 01 S 5/323

識別記号

F I  
H 01 L 21/205  
33/00  
H 01 S 3/18

テーマコード(参考)  
5 F 0 4 1  
C 5 F 0 4 5  
6 7 3 5 F 0 7 3

審査請求 有 請求項の数24 OL (全 9 頁)

(21)出願番号

特願平11-27009

(22)出願日

平成11年2月4日(1999.2.4)

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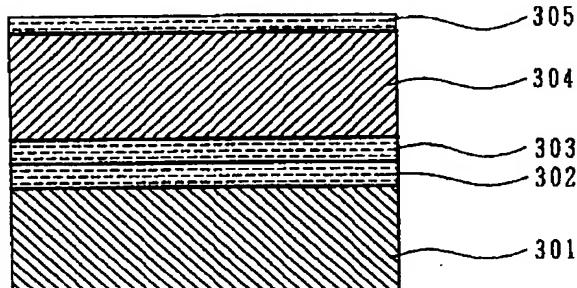
(54)【発明の名称】 気相エピタキシャル成長法、半導体基板の製造方法、半導体基板及びハイドライド気相エピタキシー装置

(57)【要約】

【課題】 高品質で量産性に優れたAlGaN基板の製造方法を提供する。

【解決手段】 c面サファイア基板301上に、減圧ハイドライドVPE法により $4 \mu\text{m}/\text{h}$ 以下の成長速度で薄いGaN層302を成長させた後、このGaN層302上に常圧ハイドライドVPE法により $4 \mu\text{m}/\text{h}$ よりも大きく且つ $200 \mu\text{m}/\text{h}$ 以下の成長速度で十分に厚いAlGaN層304を成長させる。次に、c面サファイア基板1をエッチングにより除去し、GaN層302、AlGaN層303、304からなるAlGaN基板を得る。

【効果】 減圧ハイドライドVPE法により、成長速度が小さくなり且つIII族原料分子の表面マイグレーションが促進され、良好な品質の結晶が得られる。更に、連続して常圧ハイドライドVPE法を行うことにより、大きな成長速度でGaNおよびAlGaNを成長させるため高品質で量産性に優れたAlGaN基板が得られる。



## 【特許請求の範囲】

【請求項1】 厚さd<sub>1</sub>の基板上に、成長速度V<sub>2</sub>、成長圧力P<sub>2</sub>の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d<sub>2</sub>成長させた後、前記基板を装置外に取り出すことなく、成長速度V<sub>3</sub>、成長圧力P<sub>3</sub>の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d<sub>3</sub>成長させるプロセスを含む気相エピタキシャル成長法において、V<sub>2</sub><V<sub>3</sub>、且つP<sub>2</sub><P<sub>3</sub>、且つd<sub>2</sub><d<sub>3</sub>なる条件を満たすことを特徴とする気相エピタキシャル成長法。

【請求項2】 前記第1の半導体層の成長温度T<sub>2</sub>、第2の半導体層の成長温度T<sub>3</sub>が、T<sub>2</sub><T<sub>3</sub>なる条件を満たすことを特徴とする請求項1記載の気相エピタキシャル成長法。

【請求項3】 前記気相エピタキシャル成長法が、ハイドライド気相エピタキシャル成長法或いは有機金属気相エピタキシャル成長法であることを特徴とする請求項1又は2記載の気相エピタキシャル成長法。

【請求項4】 成長速度V<sub>2</sub>、V<sub>3</sub>が夫々、0μm/h<V<sub>2</sub><4μm/h、4μm/h<V<sub>3</sub><400μm/hなる条件を満たすことを特徴とする請求項1乃至3の何れかに記載の気相エピタキシャル成長法。

【請求項5】 成長圧力P<sub>2</sub>、P<sub>3</sub>が夫々、1torr<P<sub>2</sub><200torr、200torr<P<sub>3</sub><1000torrなる条件を満たすことを特徴とする請求項1乃至4の何れかに記載の気相エピタキシャル成長法。

【請求項6】 成長層厚d<sub>2</sub>、d<sub>3</sub>が夫々、0nm<d<sub>2</sub><500nm、10μm<d<sub>3</sub><1mmなる条件を満たすことを特徴とする請求項1乃至5の何れかに記載の気相エピタキシャル成長法。

【請求項7】 成長温度T<sub>2</sub>、T<sub>3</sub>が夫々、400°C<T<sub>2</sub><700°C、700°C<T<sub>3</sub><1200°Cなる条件を満たすことを特徴とする請求項1乃至6の何れかに記載の気相エピタキシャル成長法。

【請求項8】 前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とする請求項1乃至7の何れかに記載の気相エピタキシャル成長法。

【請求項9】 前記第1の半導体層或いは第2の半導体層の少なくとも1つの層がB<sub>x1</sub>A<sub>1-y1</sub>G<sub>a<sub>z1</sub></sub>In<sub>1-x1-y1-z1</sub>N(0≤X<sub>1</sub>, Y<sub>1</sub>, Z<sub>1</sub>≤1)であることを特徴とする請求項1乃至8の何れかに記載の気相エピタキシャル成長法。

【請求項10】 前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層がA<sub>1-x2</sub>G<sub>a<sub>1-x2</sub></sub>N(0≤X<sub>2</sub>≤1)であり、前記第2の半導体層の少なくとも1つの層がA<sub>1-y2</sub>G<sub>a<sub>1-y2</sub></sub>N(0≤Y<sub>2</sub>≤1)であることを特徴とする請求項1乃至9の何れかに記載の気相エピタキシャル成長法。

【請求項11】 前記第1の半導体層がGaN或いはAlN

1N或いはGaN/A1N超格子であり、前記第2の半導体層がA<sub>1-y3</sub>G<sub>a<sub>1-y3</sub></sub>N(0.05≤Y<sub>3</sub>≤0.5)であることを特徴とする請求項9乃至11の何れかに記載の気相エピタキシャル成長法。

【請求項12】 厚さd<sub>1</sub>の基板上に、成長速度V<sub>2</sub>、成長圧力P<sub>2</sub>の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d<sub>2</sub>成長させた後、前記基板を装置外に取り出すことなく、成長速度V<sub>3</sub>、成長圧力P<sub>3</sub>の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d<sub>3</sub>成長させるプロセスを含む気相エピタキシャル成長法において、V<sub>2</sub><V<sub>3</sub>、且つP<sub>2</sub><P<sub>3</sub>、且つd<sub>2</sub><d<sub>3</sub>なる条件を満たすことを特徴とする気相エピタキシャル成長法。

V<sub>2</sub><V<sub>3</sub>、且つP<sub>2</sub><P<sub>3</sub>、且つd<sub>2</sub><d<sub>3</sub>なる条件を満たす気相エピタキシャル成長法によって形成されたウエハから前記基板を除去して得られる前記第1の半導体層と第2の半導体層とからなる半導体基板の製造方法。

【請求項13】 更に、前記第1の半導体層又は第2の半導体層の何れかを除去したことを特徴とする請求項12記載の半導体基板の製造方法。

【請求項14】 前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とする請求項12又は13記載の半導体基板の製造方法。

【請求項15】 前記第1の半導体層或いは第2の半導体層の少なくとも1つの層がB<sub>x1</sub>A<sub>1-y1</sub>G<sub>a<sub>z1</sub></sub>In<sub>1-x1-y1-z1</sub>N(0≤X<sub>1</sub>, Y<sub>1</sub>, Z<sub>1</sub>≤1)であることを特徴とする請求項12乃至14の何れかに記載の半導体基板の製造方法。

【請求項16】 前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層がA<sub>1-x2</sub>G<sub>a<sub>1-x2</sub></sub>N(0≤X<sub>2</sub>≤1)であり、前記第2の半導体層の少なくとも1つの層がA<sub>1-y2</sub>G<sub>a<sub>1-y2</sub></sub>N(0≤Y<sub>2</sub>≤1)であることを特徴とする請求項12乃至15の何れかに記載の半導体基板の製造方法。

【請求項17】 前記第1の半導体層がGaN或いはAlN或いはGaN/A1N超格子であり、前記第2の半導体層がA<sub>1-y3</sub>G<sub>a<sub>1-y3</sub></sub>N(0.05≤Y<sub>3</sub>≤0.5)であることを特徴とする請求項12乃至16の何れかに記載の半導体基板の製造方法。

【請求項18】 前記基板の厚さd<sub>1</sub>と前記第2の半導体層の層厚d<sub>3</sub>との関係が、d<sub>1</sub><d<sub>3</sub>であることを特徴とする請求項13乃至17の何れかに記載の半導体基板の製造方法。

【請求項19】 厚さd<sub>1</sub>の基板上に第1の半導体層を層厚d<sub>2</sub>成長させた後、第2の半導体層を層厚d<sub>3</sub>を気相エピタキシャル成長法で成長させ、d<sub>2</sub><d<sub>3</sub>なる条件を満たす半導体基板であって、前記第1の半導体層或いは第2の半導体層3少なくとも1つの層がB<sub>x1</sub>A<sub>1-y1</sub>G<sub>a<sub>z1</sub></sub>In<sub>1-x1-y1-z1</sub>N(0≤X<sub>1</sub>, Y<sub>1</sub>, Z<sub>1</sub>≤1)であることを特徴とする半導体基板。

【請求項20】 厚さd1の基板上に第1の半導体層を層厚d2成長させた後、第2の半導体層を層厚d3を気相エピタキシャル成長法で成長させ、d2<d3なる条件を満たす半導体基板であって、

前記基板がサファイア或いはSi或いはGaNであり、前記第1の半導体層の少なくとも1つの層がA<sub>1-x<sub>2</sub></sub>G<sub>a<sub>1-x<sub>2</sub></sub>N</sub>(0≤X<sub>2</sub>≤1)であり、前記第2の半導体層の少なくとも1つの層がA<sub>1-y<sub>2</sub></sub>G<sub>a<sub>1-y<sub>2</sub></sub>N</sub>(0≤Y<sub>2</sub>≤1)であることを特徴とする導体基板。

【請求項21】 厚さd1の基板上に第1の半導体層を層厚d2成長させた後、第2の半導体層を層厚d3を気相エピタキシャル成長法で成長させ、d2<d3なる条件を満たす半導体基板であって、

前記第1の半導体層がGaN或いはAlN或いはGaN/A<sub>1</sub>N超格子であり、前記第2の半導体層がA<sub>1-y<sub>2</sub></sub>G<sub>a<sub>1-y<sub>2</sub></sub>N</sub>(0.05≤Y<sub>2</sub>≤0.5)であることを特徴とする半導体基板。

【請求項22】 前記基板の厚さd1と前記第2の半導体層の層厚d3との関係が、d1<d3であることを特徴とする請求項19乃至21の何れかに記載の半導体基板。

【請求項23】 前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とする請求項19乃至22の何れかに記載の半導体基板。

【請求項24】 サファイア製の反応管或いは基板を取り囲むように設置されたサファイア製の内挿管を有し、Alを含む結晶の成長を可能にすると共に、10torr以上800torr未満の圧力で成長可能にしたことを特徴とするハイドライド気相エピタキシー装置。

#### 【発明の詳細な説明】

##### 【0001】

【発明の属する技術分野】本発明は、気相エピタキシャル成長法、半導体基板の製造方法、半導体基板及びハイドライド気相エピタキシー(VPE)装置に係わり、特に、高品質、且つ、量産性に優れたGaN基板やAlGaN基板等の窒化物系III-V族化合物半導体膜等の半導体の気相エピタキシャル成長法、半導体基板の製造方法、半導体基板とその成長装置に関する。

##### 【0002】

【従来の技術】近年、光ディスクや光磁気ディスクに対する記録、再生の高密度化、高解像度化の要求から、短波長の青色や紫外線発光の半導体レーザダイオード(LD)の開発がなされている。例えば、1994年2月の日経エレクトロニクス602号の93ページには日亜化学の中村氏による青色発光ダイオードの解説がある。

【0003】窒化物系III-V族化合物半導体であるGaNは、禁制帯幅が3.4eVと大きくしかも直接遷移型であることから、青色、紫外線発光素子用材料として注目されている。従来、窒化物系III-V族化合物半導体結晶の成長には、基板材料としてサファイアが多

く用いられている。サファイア基板上へのGaN膜の成長は900~1100°Cの高温で有機金属気相エピタキシャル成長(MOVPE)法や分子線エピタキシー(MBE)法により行われている。既にデバイスレベルの結晶品質を有する膜が得られているが、サファイア基板とGaNエピタキシャル層は格子定数や熱膨張係数が異なっていることにより、欠陥が生成されたり、クラックが発生したりするなどの問題があり、素子の特性や信頼性を低下させている。

【0004】更に、サファイア基板は、へき開性に乏しく加工性が悪いため、LDに必要なミラー面の形成やチップ化が難しい。また、サファイアは、電気的に絶縁性であるため、素子の電極形成には選択エッチングなどの複雑なプロセスを必要とする。GaN厚膜基板は、GaNエピタキシャル層と格子定数や熱膨張係数が一致していることにより、欠陥が生成されたりクラックが発生したりするなどの問題がないので、理想的な基板材料である。これにより、LDの共振器端面を劈開により形成することができ、基板の裏面に電極を形成することができる。素子の特性や信頼性を向上させることができる。

【0005】しかし、GaNの厚膜基板を製造するには、窒素の蒸気圧が高いことにより、Si基板やGaN基板などの製造に一般に用いられている方法は用いることができない。GaNの成長方法としては、MOCVD法やMBE法以外に、ハイドライド(水素化物)を原料として用いるハイドライド気相エピタキシー(VPE)法が知られていて、特開平10-173288号公報には、「窒化物系III-V族化合物半導体層の成長方法および窒化物系III-V族化合物半導体基板の製造方法」なる発明が開示されている。このハイドライドVPE法によれば、サファイア基板上に1時間に数~数百μmの厚さのGaN層を常圧で成長させることができると、GaN基板を製造する有効な方法の一つと考えられる。

【0006】しかしながら、この方法で得られたGaN基板は、結晶性や表面状態が悪かったり、GaN層が基板に垂直ではなく斜めに成長することから、基板として用いるのには品質が不十分であった。その理由は、常圧ハイドライドVPE法は成長速度が大きいため、優れた結晶品質のGaNが得られないからである。また、AlGaN基板が得られれば、LDのクラッド層に基板と同じAl組成の高品質のAlGaNを用いることができる。GaN基板上のLDより、さらに効率よく活性層に光を閉じ込めることができ、LDの特性を大きく向上させることができる。

【0007】しかし、常圧ハイドライドVPE法は成長速度が大きいため、塩化アルミ(AlCl<sub>3</sub>)などのAlを含む原料の結晶表面でのマイグレーションが極めて小さくなり、高品質のエピタキシャル結晶が得られない。その上、ハイドライドVPE法では、塩化アルミな

どのAlを含む原料が石英反応管を腐食するという問題があり、安全且つ安定した成長が困難であった。また、石英反応管から出た酸素がエピタキシャル層に取り込まれ、結晶品質を低下させるという問題もあった。

## 【0008】

【発明が解決しようとする課題】本発明の目的は、上記した従来技術の欠点を改良し、特に、減圧ハイドライドVPE法により、成長速度が小さくなり、且つ、III族原料分子の表面マイグレーションが促進され、良好な品質の結晶が得られ、その上、連続した常圧ハイドライドVPE法により、大きな成長速度でGaNおよびAlGaNを成長させることを可能にした高品質で量産性に優れた新規な半導体の気相エピタキシャル成長法、半導体基板の製造方法、半導体基板とその成長装置を提供するものである。

## 【0009】

【課題を解決するための手段】本発明は上記した目的を達成するため、基本的には、以下に記載されたような技術構成を採用するものである。即ち、本発明に係わる気相エピタキシャル成長法の第1態様は、厚さd1の基板上に、成長速度V2、成長圧力P2の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d2成長させた後、前記基板を装置外に取り出すことなく、成長速度V3、成長圧力P3の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d3成長させるプロセスを含む気相エピタキシャル成長法において、 $V_2 < V_3$ 、且つ $P_2 < P_3$ 、且つ $d_2 < d_3$ なる条件を満たすことを特徴とするものであり、又、第2態様は、前記第1の半導体層の成長温度T2、第2の半導体層の成長温度T3が、 $T_2 < T_3$ なる条件を満たすことを特徴とするものであり、又、第3態様は、前記気相エピタキシャル成長法が、ハイドライド気相エピタキシャル成長法あるいは有機金属気相エピタキシャル成長法であることを特徴とするものであり、又、第4態様は、成長速度V2、V3が夫々、 $0 \mu\text{m}/\text{h} < V_2 < 4 \mu\text{m}/\text{h}$ 、 $4 \mu\text{m}/\text{h} < V_3 < 400 \mu\text{m}/\text{h}$ なる条件を満たすことを特徴とするものであり、又、第5態様は、成長圧力P2、P3が夫々、 $1 \text{ torr} < P_2 < 200 \text{ torr}$ 、 $200 \text{ torr} < P_3 < 1000 \text{ torr}$ なる条件を満たすことを特徴とするものであり、又、第6態様は、成長層厚d2、d3が夫々、 $0 \text{ nm} < d_2 < 500 \text{ nm}$ 、 $10 \mu\text{m} < d_3 < 1 \text{ mm}$ なる条件を満たすことを特徴とするものであり、又、第7態様は、成長温度T2、T3が夫々、 $400^\circ\text{C} < T_2 < 700^\circ\text{C}$ 、 $700^\circ\text{C} < T_3 < 1200^\circ\text{C}$ なる条件を満たすことを特徴とするものであり、又、第8態様は、前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とするものであり、又、第9態様は、前記第1の半導体層或いは第2の半導体層の少なくとも1つの層が $B_{x_1}A_{1-y_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$  ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ) であ

ることを特徴とするものであり、又、第10態様は、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層が $A_{1-x_2}Ga_{x_2}N$  ( $0 \leq X_2 \leq 1$ ) であり、前記第2の半導体層の少なくとも1つの層が $A_{1-y_2}Ga_{y_2}N$  ( $0 \leq Y_2 \leq 1$ ) であることを特徴とするものであり、又、第11態様は、前記第1の半導体層がGaN或いはAlN或いはGaN/A1N超格子であり、前記第2の半導体層が $A_{1-y_3}Ga_{y_3}N$  ( $0.05 \leq Y_3 \leq 0.5$ ) であることを特徴とするものである。

【0010】又、本発明に係わる半導体基板の製造方法の第1態様は、厚さd1の基板上に、成長速度V2、成長圧力P2の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d2成長させた後、前記基板を装置外に取り出すことなく、成長速度V3、成長圧力P3の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d3成長させるプロセスを含む気相エピタキシャル成長法において、 $V_2 < V_3$ 、且つ $P_2 < P_3$ 、且つ $d_2 < d_3$ なる条件を満たす気相エピタキシャル成長法によって形成されたウェハから前記基板を除去して得られる前記第1の半導体層と第2の半導体層とからなるものであり、又、第2態様は、更に、前記第1の半導体層又は第2の半導体層の何れかを除去したことを特徴とするものであり、又、第3態様は、前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とするものであり、又、第4態様は、前記第1の半導体層或いは第2の半導体層の少なくとも1つの層が $B_{x_1}A_{1-y_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$  ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ) であることを特徴とするものであり、又、第5態様は、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層が $A_{1-x_2}Ga_{x_2}N$  ( $0 \leq X_2 \leq 1$ ) であり、前記第2の半導体層の少なくとも1つの層が $A_{1-y_2}Ga_{y_2}N$  ( $0 \leq Y_2 \leq 1$ ) であることを特徴とするものであり、又、第6態様は、前記第1の半導体層がGaN或いはAlN或いはGaN/A1N超格子であり、前記第2の半導体層が $A_{1-y_3}Ga_{y_3}N$  ( $0.05 \leq Y_3 \leq 0.5$ ) であることを特徴とするものであり、又、第7態様は、前記基板の厚さd1と前記第2の半導体層の層厚d3との関係が、 $d_1 < d_3$ であることを特徴とするものである。

【0011】又、本発明に係わる半導体基板の第1態様は、厚さd1の基板上に第1の半導体層を層厚d2成長させた後、第2の半導体層を層厚d3を気相エピタキシャル成長法で成長させ、 $d_2 < d_3$ なる条件を満たす半導体基板であって、前記第1の半導体層或いは第2の半導体層3少なくとも1つの層が $B_{x_1}A_{1-y_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$  ( $0 \leq X_1, Y_1, Z_1 \leq 1$ ) であることを特徴とするものであり、又、第2態様は、厚さd1の基板上に第1の半導体層を層厚d2成長させた後、第2

の半導体層を層厚d<sub>3</sub>を気相エピタキシャル成長法で成長させ、d<sub>2</sub> < d<sub>3</sub>なる条件を満たす半導体基板であって、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層がA<sub>1-x</sub>G<sub>x</sub>A<sub>1-y</sub>N (0 ≤ X ≤ 1)であり、前記第2の半導体層の少なくとも1つの層がA<sub>1-y</sub>G<sub>x</sub>A<sub>1-z</sub>N (0 ≤ Y ≤ 1)であることを特徴とするものであり、又、第3態様は、厚さd<sub>1</sub>の基板上に第1の半導体層を層厚d<sub>2</sub>成長させた後、第2の半導体層を層厚d<sub>3</sub>を気相エピタキシャル成長法で成長させ、d<sub>2</sub> < d<sub>3</sub>なる条件を満たす半導体基板であって、前記第1の半導体層がGaN或いはAlN或いはGaN/A<sub>1</sub>N超格子であり、前記第2の半導体層がA<sub>1-y</sub>G<sub>x</sub>A<sub>1-z</sub>N (0.05 ≤ Y ≤ 0.5)であることを特徴とするものであり、又、第4態様は、前記基板の厚さd<sub>1</sub>と前記第2の半導体層の層厚d<sub>3</sub>との関係が、d<sub>1</sub> < d<sub>3</sub>であることを特徴とするものであり、又、第5態様は、前記第1の半導体層と第2の半導体層と共にn型或いは共にp型であることを特徴とするものである。

【0012】又、本発明に係わるハイドライド気相エピタキシー装置の態様は、サファイア製の反応管或いは基板を取り囲むように設置されたサファイア製の内挿管を有し、Alを含む結晶の成長を可能にすると共に、10 torr以上800 torr未満の圧力で成長可能にしたことを特徴とするものである。

#### 【0013】

【発明の実施の形態】本発明に係わる半導体基板は、c面サファイア基板301上に、減圧ハイドライドVPE法により4 μm/h以下の成長速度で薄いGaN層302を成長させた後、このGaN層302上に常圧ハイドライドVPE法により4 μm/hよりも大きくかつ400 μm/h以下の成長速度で十分に厚いAlGaN層304を成長させる結晶成長法、或いは、c面サファイア基板1をエッチングにより除去し、GaN層302とAlGaN層304からなるAlGaN基板、或いは、AlGaN層304のみからなるAlGaN基板、或いは、サファイア製の内挿管又はサファイア製の反応管を有するAlを含む結晶が成長できる10 torr以上800 torr未満の圧力で成長可能なハイドライドVPE装置である。

【0014】減圧ハイドライドVPE法により、成長速度が小さくなり且つAlなどのIII族原料分子の表面マイグレーションが促進され、良好な品質の結晶が得られる。その上に、エピタキシャル基板を装置外に出さずに連続して、圧力を大きくして、常圧ハイドライドVPE法を用いることで、大きな成長速度でAlGaNを成長させることができ、高品質のAlGaN基板が効率よく得られる。

#### 【0015】

【実施例】以下に、本発明に係わる半導体の気相エピタ

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キシャル成長法、半導体基板の製造方法、半導体基板及びその成長装置の具体例を図面を参照しながら詳細に説明する。図1、図2に本発明のハイドライドVPE装置の側面図と正面図を示す。

【0016】本発明の第1の具体例のハイドライドVPE装置は、サファイア製反応管100と、サファイア製反応管100内に設けられたサファイア製内挿管101と、サファイア製内挿管101内の基板を成長室に入れたり、待機室に移動させたり操作する基板操作ロッド102と、排気口116に設けられたロータリーポンプ103と、圧力調節弁104と、基板操作ロッド102で操作されるヒータ付き基板ホルダ105と、基板ホルダ105に固定される基板106と、サファイア製反応管100を囲むように設けた加熱ヒータ107と、サファイア製内挿管101内に設けられた待機室108と、前記待機室108と成長室を仕切るためのサファイア製仕切り板109と、サファイア製内挿管101内にガスを導入するため、内挿管101の一方の端部に設けたガス導入口110とガス導入管111とガス導入口112と、成長室の高純度GaNソース113と、ソースを収納するヒータ付き原料ポート114と、成長室115と、内挿管101の他方の端部に設けた排気口116と、サファイア製内挿管101の底部に設けられるサファイア製底板200と、成長室115の高純度Alソース202とから構成されている。

【0017】ガス導入口110とガス導入管111はアンモニアガスと窒素ガスを導入するためのガス導入口とガス導入管である。ガス導入口112はHClガスと水素ガスを導入するガス導入口である。各種のガス供給量は流量計と調節弁で制御されている。基板はサファイア、シリコン、GaAsなどの基板である。nドーパント原料にはSiH<sub>4</sub>やSiH<sub>2</sub>C<sub>2</sub>ガスを用い、pドーパント原料にはMg(CH<sub>3</sub>)<sub>2</sub>やMgC<sub>2</sub>を用い、ガス導入管111を通して供給する。

【0018】本発明のハイドライドVPE装置は、サファイア製の反応管100、内挿管101、仕切り板109、仕切り板205を用い、高純度GaNソース113と高純度Alソース202の2種類の固体原料を用い、加熱ヒータ107とヒータ付き原料ポート114により高純度GaNソース113と高純度Alソース202の温度を独立に制御できるように構成され、ヒータ付き基板ホルダ105により基板温度を室温から1200°Cまで制御できる。更に、ロータリーポンプ103と圧力調節弁104によりサファイア製の反応管100内の圧力を10 torr以上800 torr以下圧力範囲で調節可能に構成したものである。

【0019】サファイア製の反応管100内は、サファイア製仕切り板109で待機室108と成長室115に分けられており、基板操作ロッド102を用いて、待機室108から成長室115に或いは逆に、基板106の

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位置を自由に変えることができる。ガス導入口112(図2では206と207で示した)から成長室115に導入されたHC1ガスは、高純度Gaソース113と高純度Alソース202とが反応して塩化ガリウム(GaCl<sub>x</sub>)と塩化アルミニウム(AlCl<sub>x</sub>)を発生し、水素ガスとともに基板表面に運ばれ、ガス導入管111から供給されるアンモニアガスと基板表面で反応し、AlGaNが成長する。AlGaNのAl組成と成長速度は、ガス導入口206とガス導入口207から導入されたHC1ガスの流量と高純度Gaソース113と高純度Alソース202との温度によって決まる。

【0020】以下に、上記した成長装置による本発明の成長方法について説明する。サファイア基板106を待機室108に設置して、ガス導入口110から窒素ガスを導入した状態で、成長温度まで基板温度を上げる。反応管内の圧力と塩化ガリウム或いは塩化アルミニウムの流量が安定したら、待機室108から成長室115に基板106の位置を変えて成長を行う。組成が異なる半導体層を成長する時は、いったん基板を待機室108に移して、水素流量や塩化ガリウム或いは塩化アルミニウムの流量や圧力を変えて、流量と圧力とが安定してから、再び成長室115に戻して成長を行う。このようにして、GaNやAlNも同様にして成長できる。基板温度が高く待機室108にエピタキシャル基板がある時は、アンモニアガスを導入し、基板からの窒素抜けを防ぐ。

【0021】図3に本発明の第2の具体例のエピタキシャル基板を示す。このエピタキシャル基板は、厚さ100μmのサファイア基板301と、厚さ50nmの減圧低温低速成長のアンドープGaN薄膜層302と、厚さ100nmの減圧高温低速成長のn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N薄膜層303と、厚さ200μmの常圧高温高速成長のn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N厚膜層304と、厚さ10nmの常圧高温中速成長のn-GaN薄膜保護層305とからなる。n濃度は5×10<sup>17</sup>cm<sup>-3</sup>である。

【0022】図5に本発明の第2の具体例の成長条件の時間変化を示す。減圧低温低速成長の条件は成長温度500°C、成長圧力50torr、成長速度0.1μm/hである。減圧高温中速成長の条件は成長温度1100°C、成長圧力50torr、成長速度1μm/hである。常圧高温高速成長の条件は成長温度1100°C、成長圧力760torr、成長速度60μm/hである。成長温度が500°Cから1100°Cに上がると原料の分解が進んで成長速度が大きくなる。高純度Gaソース113の温度は800°C、高純度Alソース202の温度は900°Cである。

【0023】上記第2の具体例の成長法は、減圧低温低速成長から減圧高温中速成長に成長温度を増大させる点に特徴が有り、更に、減圧高温中速成長から常圧高温高速成長に圧力と成長速度を同時に増大させる点に特徴が有る。減圧成長時のNH<sub>3</sub>の流量は60cc/min、Ga

へのHC1の流量は0.5cc/min、AlへのHC1の流量は0.1cc/minである。常圧成長時のNH<sub>3</sub>の流量は600cc/min、GaへのHC1の流量は5cc/min、AlへのHC1の流量は1cc/minである。

【0024】常圧(760torr)成長でのおよその各ガス分圧は、H<sub>2</sub>分圧734torr、NH<sub>3</sub>分圧20torr、GaCl<sub>x</sub>分圧5torr、AlCl<sub>x</sub>分圧1torrである。減圧(50torr)成長でのおよその各ガス分圧は、H<sub>2</sub>分圧47torr、NH<sub>3</sub>分圧2torr、GaCl<sub>x</sub>分圧0.5torr、AlCl<sub>x</sub>分圧0.1torrである。

【0025】図4に本発明の第2の具体例のAlGaN基板を示す。第2の具体例のAlGaN基板は上記エピタキシャル基板からサファイア基板301と、減圧低温中速成長のGaN薄膜層302とをエッチングで取り除いたものである。エッチングは、例えば、磷酸：硫酸=2:3のエッチャントで300°Cの温度で行う。第2の具体例のAlGaN基板は、厚さ100nmの減圧高温中速成長のn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N薄膜層401と、厚さ200μmの常圧高温高速成長のn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N厚膜層402と、厚さ10nmの常圧高温中速成長のn-GaN薄膜保護層403とからなる。

【0026】本発明は、上記の実施例の詳細に制限されるものではない。例えば、半導体層は必ずしも窒化物でなくともよく、InGaAs基板なども本発明の方法で実施できる。また、成長条件の詳細は下記に示した範囲の条件で最適化できる。例えば、成長速度を大きくしたり、成長圧力を最適化できる。半導体層の構造を超格子構造にしたりすることも可能である。基板に対する制限は特になく、サファイア基板に石英ガラスがバーナー化されて堆積されているような選択成長用基板でも適用できる。本発明のAlGaN基板のAl組成は自由に選べる。AlGaN基板に限らずGaN基板、或いはAlN基板でもよい。また、本発明の基板は、光デバイスだけでなく電子デバイス用の基板やヒートシンク材料としても使用できる。

【0027】本発明のハイドライド気相成長装置の反応管や内挿管は、石英SiO<sub>2</sub>ではなく、サファイアAl<sub>2</sub>O<sub>3</sub>で出来ているので、塩化アルミなどに対して高温での耐腐食性がある。したがって、AlGaNなどの成長温度が1000°Cを超える高温成長でも、腐食されることがないので、酸素の混入もなく、高品質の半導体膜を安全に生産できる。

【0028】図4の第2の具体例は、厚さ200μmのn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N厚膜基板である。第2の具体例の厚さ100nmのn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N薄膜層401は、減圧高温中速成長なので、Alの表面マイグレーションが促進され、高品質の膜となる。その後に成長した厚さ200μmのn-Al<sub>0.2</sub>Ga<sub>0.8</sub>N厚膜層402は成長速度が大きいが、下地の結晶品質が良いの

で、比較的高品質の膜となる作用がある。

【0029】常圧のハイドライドVPEは成長速度が特に大きく取れる特徴がある。本発明では成長速度が $60 \mu\text{m}/\text{h}$ と大きいので、約3時間で $200 \mu\text{m}$ 厚の厚膜基板が得られた。厚さ $10 \text{ nm}$ のn-GaN薄膜保護層403は、その上にAlGaN系のLDを成長するときに酸化膜の除去を容易にする作用がある。このように、本発明に係わる気相エピタキシャル成長法は、厚さd1の基板上に、成長速度V2、成長圧力P2の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d2成長させた後、前記基板を装置外に取り出すことなく、成長速度V3、成長圧力P3の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d3成長させるプロセスを含む気相エピタキシャル成長法において、 $V2 < V3$ 、且つ $P2 < P3$ 、且つ $d2 < d3$ なる条件を満たすことを特徴とするものであり、又、前記第1の半導体層の成長温度T2、第2の半導体層の成長温度T3が、 $T2 < T3$ なる条件を満たすことを特徴とするものであり、又、前記気相エピタキシャル成長法が、ハイドライド気相エピタキシャル成長法を用いたが、有機金属気相エピタキシャル成長法で成長させるようにしても良い。

【0030】又、本発明に係わる気相エピタキシャル成長法は、成長速度V2、V3が夫々、 $0 \mu\text{m}/\text{h} < V2 < 4 \mu\text{m}/\text{h}$ 、 $4 \mu\text{m}/\text{h} < V3 < 400 \mu\text{m}/\text{h}$ なる条件を満たすことを特徴とするものである。なお、発明者の実験結果では、減圧成長で、高品質の結晶が得られた最大の成長速度は、 $4 \mu\text{m}/\text{h}$ であり、常圧成長で、高品質の結晶が得られた最大の成長速度は、 $400 \mu\text{m}/\text{h}$ であった。

【0031】又、成長圧力P2、P3が夫々、 $1 \text{ torr} < P2 < 200 \text{ torr}$ 、 $200 \text{ torr} < P3 < 1000 \text{ torr}$ なる条件を満たすことを特徴とするものであり、発明者の実験結果では、上記範囲でのみ高品質の結晶が得られた。又、成長層厚d2、d3が夫々、 $0 \text{ nm} < d2 < 500 \text{ nm}$ 、 $10 \mu\text{m} < d3 < 1 \text{ mm}$ なる条件を満たすことを特徴とするものである。

【0032】なお、GaN系の場合、低温成長のバッファ層(厚さd2)として、 $0.05 \sim 0.5 \mu\text{m}$ の厚さのものを用いると、最も高品質のエピタキシャル結晶が得られた。又、成長温度T2、T3が夫々、 $400^\circ\text{C} < T2 < 700^\circ\text{C}$ 、 $700^\circ\text{C} < T3 < 1200^\circ\text{C}$ なる条件を満たすことを特徴とするものである。

【0033】実験では、 $400^\circ\text{C} < T2 < 700^\circ\text{C}$ の温度範囲でバッファ層を成長させると、結晶の2次元化が進行し、表面が平坦なエピタキシャル結晶が得られた。又、T3が $1200^\circ\text{C}$ 以上では、N原子がGaN層から抜け出してしまい、良好な結晶が得られない傾向があり、一方、T3が $700^\circ\text{C}$ 以下の場合も、良好な結晶が得られなかった。

【0034】又、前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とするものであり、又、前記第1の半導体層或いは第2の半導体層の少なくとも1つの層が $B_{x_1}A_{1-x_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$ ( $0 \leq X_1, Y_1, Z_1 \leq 1$ )であっても良い。更に、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層が $A_{1-x_2}Ga_{x_2}N$ ( $0 \leq X_2 \leq 1$ )であり、前記第2の半導体層の少なくとも1つの層が $A_{1-y_2}Ga_{1-y_2}N$ ( $0 \leq Y_2 \leq 1$ )であることを特徴とするものであり、又、前記第1の半導体層がGaN或いはAlN或いはGaN/A1N超格子であり、前記第2の半導体層が $A_{1-y_3}Ga_{1-y_3}N$ ( $0.05 \leq Y_3 \leq 0.5$ )であっても良い。

【0035】又、本発明に係わる半導体基板の製造方法は、厚さd1の基板上に、成長速度V2、成長圧力P2の成長条件で少なくとも1つの層からなる第1の半導体層を層厚d2成長させた後、前記基板を装置外に取り出すことなく、成長速度V3、成長圧力P3の成長条件で少なくとも1つの層からなる第2の半導体層を層厚d3成長させるプロセスを含む気相エピタキシャル成長法において、 $V2 < V3$ 、且つ $P2 < P3$ 、且つ $d2 < d3$ なる条件を満たす気相エピタキシャル成長法によって形成されたウエハから前記基板を除去して得られる前記第1の半導体層と第2の半導体層とからなるものであり、又、更に、前記第1の半導体層又は第2の半導体層の何れかを除去したことを特徴とするものであり、又、前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とするものであり、又、前記第1の半導体層或いは第2の半導体層の少なくとも1つの層が $B_{x_1}A_{1-x_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$ ( $0 \leq X_1, Y_1, Z_1 \leq 1$ )であることを特徴とするものであり、又、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層が $A_{1-x_2}Ga_{x_2}N$ ( $0 \leq X_2 \leq 1$ )であり、前記第2の半導体層の少なくとも1つの層が $A_{1-y_2}Ga_{1-y_2}N$ ( $0 \leq Y_2 \leq 1$ )であることを特徴とするものであり、又、前記第1の半導体層がGaN或いはAlN或いはGaN/A1N超格子であり、前記第2の半導体層が $A_{1-y_3}Ga_{1-y_3}N$ ( $0.05 \leq Y_3 \leq 0.5$ )であることを特徴とするものであり、又、前記基板の厚さd1と前記第2の半導体層の層厚d3との関係が、 $d1 < d3$ であることを特徴とするものである。

【0036】又、本発明に係わる半導体基板は、厚さd1の基板上に第1の半導体層を層厚d2成長させた後、第2の半導体層を層厚d3を気相エピタキシャル成長法で成長させ、 $d2 < d3$ なる条件を満たす半導体基板であって、前記第1の半導体層或いは第2の半導体層の少なくとも1つの層が $B_{x_1}A_{1-x_1}Ga_{z_1}In_{1-x_1-y_1-z_1}N$ ( $0 \leq X_1, Y_1, Z_1 \leq 1$ )であることを特徴とする

ものであり、又、厚さ  $d_1$  の基板上に第1の半導体層を層厚  $d_2$  成長させた後、第2の半導体層を層厚  $d_3$  を気相エピタキシャル成長法で成長させ、 $d_2 < d_3$  なる条件を満たす半導体基板であって、前記基板がサファイア或いはSi或いはGaAsであり、前記第1の半導体層の少なくとも1つの層が  $A_{1-x}G_{x-y}N$  ( $0 \leq x \leq 1$ ) であり、前記第2の半導体層の少なくとも1つの層が  $A_{1-y}G_{y-z}N$  ( $0 \leq y \leq 1$ ) であることを特徴とするものであり、又、厚さ  $d_1$  の基板上に第1の半導体層を層厚  $d_2$  成長させた後、第2の半導体層を層厚  $d_3$  を気相エピタキシャル成長法で成長させ、 $d_2 < d_3$  なる条件を満たす半導体基板であって、前記第1の半導体層が GaN 或いは AlN 或いは GaN/A1N 超格子であり、前記第2の半導体層が  $A_{1-y}G_{y-z}N$  ( $0.05 \leq y \leq 0.5$ ) であることを特徴とするものであり、又、前記基板の厚さ  $d_1$  と前記第2の半導体層の層厚  $d_3$  との関係が、 $d_1 < d_3$  であることを特徴とするものであり、又、前記第1の半導体層と第2の半導体層とが共にn型或いは共にp型であることを特徴とするものである。

【0037】又、本発明に係るハイドライド気相エピタキシーアー装置の態様は、サファイア製の反応管或いは基板を取り囲むように設置されたサファイア製の内挿管を有し、Alを含む結晶の成長を可能にすると共に、10 torr以上800 torr未満の圧力で成長可能にしたことを見出するものである。

#### 【0038】

【発明の効果】本発明の成長法は、高品質のn-AlGaN厚膜基板を効率良く生産できる。又、本発明のハイドライド気相成長装置は、Alを含む高品質の半導体膜を安全に生産できる。本発明のn-Al<sub>1-x</sub>G<sub>x</sub>N厚膜基板上にn-Al<sub>1-x</sub>G<sub>x</sub>Nクラッド、GaN或いはInGaN/GaNの多重量子井戸の活性層、p-Al<sub>1-x</sub>G<sub>x</sub>Nクラッド、p-GaNコンタクト層を順次形成し、p電極とn電極を付けるとAlGaN系のLDが得られる。AlGaN系のLDはGaN基板のものより、光閉じ込めやキャリア閉じ込めが優れているので、発光効率が高く、閾電流値の低い優れたLDが得られる。活性層への歪みも少なく放熱特性も良いので連続発振における素子の信頼性が向上する。発光波長もより短波長化できるので、光ディスクの記録密度を向上できる利点がある。

(8)  
14  
\* 【図面の簡単な説明】

【図1】本発明の第1の具体例であるハイドライドVPE装置の側面図である。

【図2】本発明の第1の具体例であるハイドライドVPE装置の正面図である。

【図3】本発明の第2の具体例のエピタキシャル基板の断面図である。

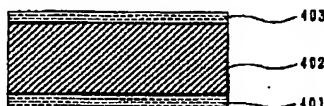
【図4】本発明の第2の具体例のAlGaN基板の断面図である。

【図5】本発明の第2の具体例の成長条件の時間変化を示すグラフである。

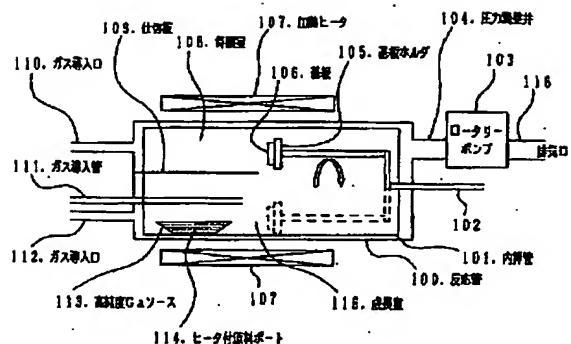
#### 【符号の説明】

|     |  |
|-----|--|
| 100 | サファイア製反応管  |
| 101 | サファイア製内挿管  |
| 102 | 基板操作ロッド  |
| 103 | ロータリーポンプ   |
| 104 | 圧力調節弁  |
| 105 | 基板ホルダ  |
| 106 | 基板   |
| 20  | 待機室  |
| 109 | サファイア製仕切り板                                       |
| 110 | ガス導入口  |
| 111 | ガス導入管  |
| 112 | ガス導入口  |
| 113 | 高純度GaNソース  |
| 114 | 原料ポート  |
| 115 | 成長室  |
| 116 | 排気口  |
| 200 | サファイア製底板   |
| 30  | 202 高純度Alソースソース                                  |
| 301 | サファイア基板  |
| 302 | 減圧低温低速成長のGaN薄膜層                                  |
| 303 | 減圧高温中速成長のn-Al <sub>1-x</sub> G <sub>x</sub> N薄膜層 |
| 304 | 常圧高温高速成長のn-Al <sub>1-x</sub> G <sub>x</sub> N厚膜層 |
| 305 | 常圧高温中速成長のn-GaN薄膜保護層                              |
| 401 | 減圧高温中速成長のn-Al <sub>1-x</sub> G <sub>x</sub> N薄膜層 |
| 402 | 常圧高温高速成長のn-Al <sub>1-x</sub> G <sub>x</sub> N厚膜層 |
| *   | 403 常圧高温中速成長のn-GaN薄膜保護層                          |

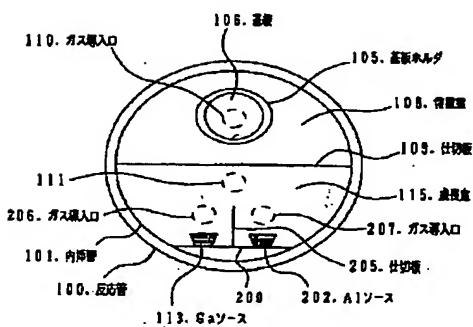
【図5】



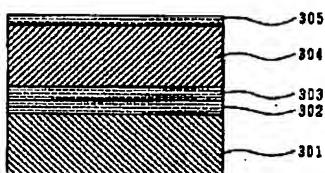
【図1】



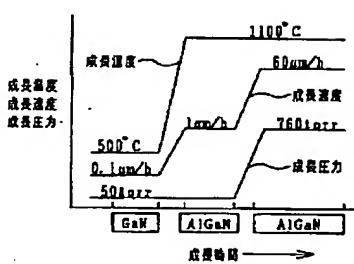
【図2】



【図3】



【図4】



フロントページの続き

Fターム(参考) 5F041 AA31 AA40 CA33 CA34 CA35  
 CA40 CA46 CA64 CA65  
 5F045 AA04 AA06 AB09 AB14 AB17  
 AB19 AC03 AC12 AC13 AD08  
 AD09 AD10 AD11 AD12 AD13  
 AD14 AD15 AD16 AE21 AE23  
 AE25 AE30 AF03 AF04 AF09  
 AF13 BB08 BB09 BB16 CA12  
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